# Solvent Extraction of Cadmium(II) with Benzoyltrifluoroacetone in the Presence of Certain Auxiliary Ligands

Roma Lahiri and G. N. Rao

Chemistry Department Indian Institute of Technology Hauz Khas, New Delhi-110016

Extraction of cadmium(II) from aqueous acetate buffered media with benzoyltrifluoroacetone (BTA) in benzene has been studied with and without the addition of auxiliary ligands like pyridine (PY), 3-methylpyridine (3MP), 4-methylpyridine (4MP), pyridine N-oxide (PO), 2-methylpyridine N-oxide (2MPO), 4-methylpyridine N-oxide (4MPO), tributylphosphate (TBP) and trioctylphosphine oxide (TOPO). Synergistic enhancement was observed in all systems. Extraction constants and adduct formation constants have been calculated. Adduct formation constants increase in the following order.

TOPO > 4MP > 3MP > PY > TBP > 4MPO > 2MPO > PO
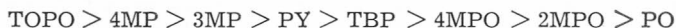
This trend follows the order of basicities of the auxiliary ligands.

INTRODUCTION

The synergistic extraction of some metal chelates with heterocyclic N-bases has been extensively investigated in recent years and the so-called synergistic effect has been attributed to the formation of an adduct by the donor molecules with the metal chelates.[1]

There are not many reports where the effect of heterocyclic N-bases is compared with that of heterocyclic base N-oxides.[2-7] In the present work, the synergistic effect of some heterocyclic N-bases, the corresponding N-oxides and some phosphorous esters on the extraction of cadmium(II) with BTA in benzene has been investigated. Cadmium chloride is a potent carcinogen and good correlation has been observed between high renal cadmium levels and hypertension.[8] As the extraction of cadmium(II) has not been investigated in detail it was considered interesting to undertake this study.
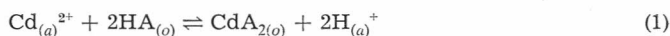
EXPERIMENTAL

PY, 3MP and 4MP were obtained from British Drug House Limited. BTA, PO, 2MPO, 4MPO were obtained from Fluka. TBP was obtained from Indian Drugs and Pharmaceuticals Limited. TOPO was obtained from Eastman Organic Chemicals; pH of the aqueous phase was maintained by using acetate buffers. A constant ionic strength of 0.1 mol dm^{-3} was maintained by using potassium nitrate solution. 10 ml of the aqueous layer containing 2 ml of 100 ppm cadmium acetate solution, 5 ml of buffer solution and 1 ml of 1 mol dm^{-3} KNO_3 solution was equilibrated with 10 ml of benzene containing BTA and the auxiliary ligand at required concentration for two hours in a thermostatic shaker at $30 \pm 1\,°C$. After equilibration the pH of the

aqueous layer was measured by an expanded scale pH meter (Electronics Corporation of India Limited). The concentration of cadmium in the aqueous phase was measured by a Pye Unicam SP 191 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Extraction mechanism was investigated by studying the distribution coefficient D_c (D_c defined as the concentration of Cd(II) in the organic phase divided by the concentration of Cd(II) in the aqueous phase) as a function of ligand concentration in the organic phase at a fixed pH value of the aqueous phase and *vice versa*. Plot of $\log D_c$ vs. pH (HA = 0.01 mol dm^{-3}) had a slope of ~ 2 and the plot of $\log D_c$ vs. $\log [HA]$ at pH 7.7 was also ~ 2. It can be inferred from these results that the main equilibrium involved in the extraction process is

$$Cd_{(a)}^{2+} + 2HA_{(o)} \rightleftharpoons CdA_{2(o)} + 2H_{(a)}^{+} \qquad (1)$$

The equilibrium constant K_{ex} (also called extraction constant) is given by

$$K_{ex} = [CdA_2]_o [H^+]_a^2/[Cd^{2+}]_a [HA]_o^2 \qquad (2)$$

making the usual approximations here[9] the value of $\log K_{ex}$ is calculated from the expression

$$\log K_{ex} = \log D_c - 2 \log [HA]_o - 2pH \qquad (3)$$

using the experimental values of D_c, [HA] and pH. The effect of adding auxiliary ligand (B) on the extraction of Cd(II) with BTA has also been investigated in a similar way determining D_c values as a function of concentration of auxiliary ligand (B) at constant pH and BTA concentration. From the plots of $\log D_c$ vs. $\log [B]_o$ the number of molecules of B incorporated in the extracted species has been determined. Extraction of Cd(II) in the presence of auxiliary ligand B may be represented by equation (4)

$$Cd_{(a)}^{2+} + 2HA_{(o)} + mB_{(o)} \rightleftharpoons CdA_2B_{m_{(o)}} + 2H_{(a)}^{+} \qquad (4)$$

With equilibrium constant K_{ex}' given by the expression

$$K_{ex}' = [CdA_2B_m]_o [H^+]_a^2/ [Cd^{2+}]_a [HA]_o^2 [B]_o^m \qquad (5)$$

and

$$\log K_{ex}' = \log D_c - 2 \log [HA]_o - 2 pH - m \log [B]_o \qquad (6)$$

K_s *i. e.* the adduct formation constant for the equilibrium

$$CdA_{2_{(o)}} + mB_{(o)} \rightleftharpoons CdA_2B_{m(o)} \qquad (7)$$

is given by the equation (8)

$$\log K_s = \log K_{ex}' - \log K_{ex} \qquad (8)$$

Since the partition coefficients of the bases in the organic solvents are low, the concentrations of the bases in the organic phase were obtained by using the formula

$$[B]_t \simeq [B]_o \left[1 + \frac{1}{P_B} + \frac{[H^+]}{P_B K_{BH}} \right] \qquad (9)$$

where P_B = partition coefficient of the base

$K_{BH} = [B] [H^+]/[BH^+]$ *i. e.* the deprotonation constant of the base. The values of P_B and pK_{BH} for the bases have been listed in Table I.[5] Adduct stability constants (K_S) and the values of K_{ex}' are listed in Table II. Figure 1 shows the

TABLE I

Partition Coefficients (P_B) and Dissociation Constants (pK_{BH}) Values of the Heterocyclic N-Bases and Heterocyclic Base N-Oxides[5]

| Auxiliary Ligand	P_B	pK_{BH}
PY	3.52	5.44
3MP	11.86	5.88
4MP	14.52	6.24
PO	0.0026	0.602
2MPO	0.0143	1.034
4MPO	0.0034	1.086

TABLE II

Extraction Constants and Formation Constants of the Adduct Formed Between the Complex Cd (BTA)$_2$ and Various Auxiliary Ligands

Auxiliary ligand	$\log K_{ex}'^*$	$\log K_s^*$
PY	—4.04	7.16
3MP	—3.8	7.4
4MP	—3.54	7.66
PO	—7.44	3.76
2MPO	—7.01	4.19
4MPO	—6.32	4.88
TBP	—4.72	6.48
TOPO	—2.72	8.48
nil	—11.2	

* Estimated uncertainty in the numerical values is ± 0.10 unit.

plots of $\log D_c$ vs. $\log [B]_o$ for PY (pH 6.45), 3MP (pH 6.4), 4MP (pH 6.4), TBP (pH 6.65) and TOPO (pH 6.16) at constant ligand concentration (0.01 mol dm^{-3}). Two moles of PY, 3MP, 4MP, TBP or TOPO are present in the extracted adduct as indicated by a slope value of ∼ 2. Figure 2 shows the plots of $\log D_c$ *vs.* $\log [B]_o$ for PO (pH 7.3), 2MPO (pH 7.2) and 4MPO (pH 7.2) at constant ligand concentration (BTA = 0.01 mol dm^{-3}). One mole of PO, 2MPO or 4MPO is present in the extracted adduct as indicated by a slope value of ∼ 1. Plots of $\log D_c$ *vs.* $\log [HA]$ at constant $[B]_o$ in all cases gave a slope of ∼ 2 indicating the presence of two moles of BTA in all these adducts. Formation constants of the adducts decreased in the following order.

TOPO > 4MP > 3MP > PY > TBP > 4MPO > 2MPO > PO
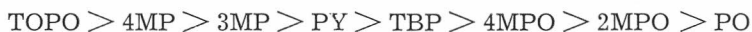
The results indicate that the formation constant of the adduct formed with an N-oxide base is smaller than that for the adduct formed with the corresponding N-base. The results are in accordance with the order of basicities of the synergists. Similar results were obtained by Al-Niami *et al.* in the
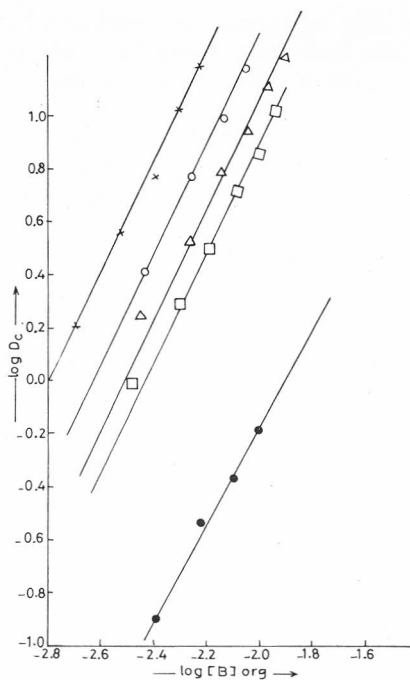
R. LAHIRI AND G. N. RAO

Figure 1. Plots of log D_c *vs.* log $[B]_o$. $\square$ = PY (pH 6.45); $\triangle$ = 3MP (pH 6.4); $\bigcirc$ = 4MP (pH 6.4); $\bullet$ = TBP (pH 6.65); $\times$ = TOPO (pH 6.16); BTA = 0.01 mol dm^{-3} in benzene. In case of TBP the vertical axis has been shifted on the positive side by 0.2 log units.
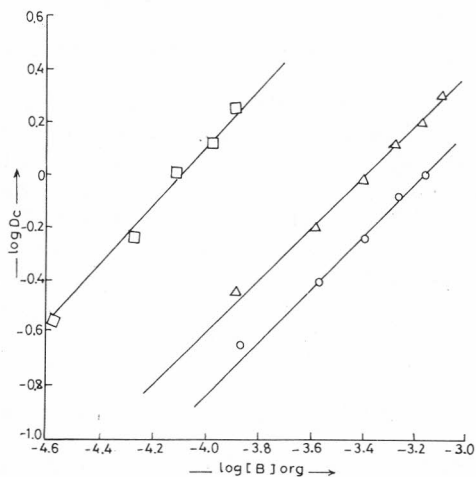

Figure 2. Plot of log D_c *vs.* log $[B]_o$. $\bigcirc$ = PO (pH 7.3); $\triangle$ = 2MPO (pH 7.2); $\square$ = 4MPO (pH 7.2); BTA = 0.01 mol dm^{-3} in benzene.

synergistic extraction studies of bis (thenoyltrifluoroacetonato) copper (II) with N-bases and N-base oxides[6]. On the other hand, formation constant of the adduct formed between bis(1-phenyl-3-methyl-4-benzoylpyrazolonato-5-)cobalt(II) and N-oxides were greater than those formed with the N-bases.[5] Such results were explained by assuming metal to ligand back bonding, which can be achieved by back donation of electrons from the filled metal d-orbitals to the empty π^* antibonding orbitals of the N—O bonds in the ligands.[5] Trioctylphosphine oxide was found to be the most effective among all the auxiliary ligands studied.

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SAŽETAK

Ekstrakcija kadmija(II) s benzoiltrifluoroacetonom uz neke pomoćne ligande

R. Lahiri i G. N. Rao

Studirana je ekstrakcija kadmija(II) iz vodenih otopina acetatnih pufera benzoiltrifluoroacetonom (BTA) u benzenu sa i bez dodatka pomoćnih liganada kao što su piridin (Py) 3-metilpiridin (3MP), 4-metilpiridin (4MP), piridin N-oksid (PO), 2-metil piridin N-oksid (2MPO), 4-metilpiridin N-oksid (4MPO), tributilfosfat (TBP) i trioktilfosfin-oksid (TOPO). Sinergički utjecaj uočen je kod svih proučavanih sistema. Izračunani su koeficijenti ekstrakcije i konstante nastajanja adukata, koje padaju u redu: TOPO > 4MP > 3MP > Py > PBP > 4MPO > 2MPO > PO. Taj je red u sukladnosti s bazičnošću liganada.